Glucose electrooxidation in alkaline medium: Performance enhancement of PdAu/C synthesized by NH$_3$ modified pulse microwave assisted polyol method

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ARTICLE INFO

ABSTRACT

Lack of highly efficient and stable electrocatalysts for glucose electrooxidation is a bottleneck for the real application of glucose fuel cells and electrochemical sensors. Herein we report the synthesis of the PdAu/C catalyst by an NH$_3$ modified pulse microwave assisted polyol method, which exhibits excellent glucose electrooxidation performance.

Both XRD and TEM results indicate that the modified method can significantly lower the particle size of the Pd, Au and PdAu nanoparticles, which can be attributed to the complexing effect of aqueous NH$_3$ with Pd^{2+} and Au^{3+} ions. The as-prepared PdAu/C-NH$_3$ shows excellent catalytic activity and high sensitivity toward glucose electrooxidation and it can be considered very promising for the potential application in the development of both glucose fuel cells and glucose sensors.

1. Introduction

Glucose electrooxidation offers a great opportunity to obtain glucose electrochemical sensors monitoring blood sugar and implantable glucose fuel cells intended for artificial hearts and heart pacer [1–9]. This makes the investigation on glucose electrooxidation a hot topic. However, it is difficult to fully oxidize glucose to CO$_2$ via transferring 24 electrons for each glucose molecule, and the kinetics for glucose electrooxidation is very sluggish on the state-of-art electrocatalysts. Therefore, it is highly desirable to develop electrocatalysts with high current and low overpotential for glucose electrooxidation and good poison tolerance is essential.

It is known that enzyme can catalyze glucose oxidation [10,11]; however, the instability of enzymes limits their long-term application in glucose oxidation [12–14]. Some noble metals (Pt, Pd and Au) and their based binary or ternary catalysts such as PtPb [15–17], AuAg [18–20], PtPd [21,22], PtBi [23,24], PtRu [23], PdRu [4], PtAu [3,24,25], PtAuPd [24,26] also possess electrocatalytic

activity to glucose oxidation. These catalysts have the advantages in stability, compatibility and long life-time compared with enzymes. At present, it is a general strategy to disperse the active components on the carbon support in terms of high utilization efficiency and electrical conductivity. In the beginning, Pt was found to have catalytic activity toward glucose electrooxidation [5,6,27,28], while the further study showed that this catalyst exhibited strong chemisorption ability for different substances in physiological solutions and poor selectivity for various organic substances [29]. These issues make Pt-based catalysts unsuitable for application in glucose electrochemical sensors for diabetes detection. Au has been found to possess better electrocatalytic activity and higher poison tolerance than Pt in neutral and alkaline solution [9,14,30–32]. On the other hand, the weak point of Au is its high overpotential for glucose electrooxidation. Compared with Pt and Au, Pd is found to exhibit superior activity toward alcohol electrooxidation in alkaline media [34]. Moreover, the abundance of Pd on the earth is at least 50 times more than that of Pt and its overpotential for glucose electrooxidation is lower than that of Au [33].

Noble metal based binary or ternary catalysts exhibit better performance than pure metals by taking advantage of each pure metal and their synergistic effect. Thus, the binary catalysts of Au and Pd are expected to be superior to Pd or Au alone in terms of the

electrocatalytic performance for glucose electrooxidation, which has been verified by our previous work [35] and other researches as well. However, the particle size of the reported PdAu/C was a little big (more than 7 nm) [35,36], which will greatly limit its catalytic activity [37]. It has been found that NH_3 possesses strong complexing ability for Pd ions, and thus avoids the formation of Pd hydroxide precipitated from Pd hydrolysis in polyol method for Pd/C catalyst preparation [38]. In the present investigation, $NH_3 \cdot H_2O$ was introduced as a mediated reagent into the pulse microwave assisted polyol method to prepare carbon supported PdAu binary catalysts. The as-prepared catalysts were characterized by *X-ray diffraction* (XRD), *transmission electron microscopy* (TEM), *scanning electron microscopy-energy dispersive spectroscopy* (SEM-EDS) and *thermogravimetry* (TG). Glucose electrooxidation on the as-prepared catalysts was evaluated by the electrochemical methods including *cyclic voltammetry* (CV) and *chronoamperometry* (CA) in the alkaline medium.

2. Experimental

2.1. Materials

Glucose (Guangzhou Chemical Reagent Corp., AR), $NH_3 \cdot H_2O$ (Guangzhou Chemical Reagent Corp., 25 wt.%), Carbon black (Vulcan XC-72R, Cabot Corp.), $HAuCl_4 \cdot 4H_2O$ (Guiyanboye Corp., AR), $PdCl_2$ (Guiyanboye Corp., AR), ethylene glycol (Shanghai Lingfeng Corp., AR), and Nafion solution (DuPont Company, 5 wt.%) were used without further purification. All other used chemicals are of analytical reagent grade. Deionized water with specific resistance more than $18.0 \, M\Omega \, cm^{-1}$ was obtained by a water purification system.

2.2. Catalyst preparation

Vulcan XC-72R carbon black supported PdAu binary catalysts with 20 wt.% noble metal was prepared through an NH_3 modified pulse microwave assisted polyol method. The detailed catalyst preparation was described as follows. A certain amount of $PdCl_2$/ethylene glycol (EG) or/and $HAuCl_4$/EG solution (for Pd/C catalyst, 2.50 mL of 12.0 mg mL^{-1} Pd^{2+}/EG solution was added; for Au/C catalyst, 3.14 mL of 9.56 mg mL^{-1} Au^{3+}/EG solution was added) was well mixed with EG, which was transparent. $NH_3 \cdot H_2O$ was added drop by drop to the above solution until the yellow

solution turned into transparent/colorless but the darker solution should be avoided. After that, 120.0 mg carbon black powder was added into the NH_3 modified metal-containing solution according to the pre-calculated metal loading (Based on our previous investigated results [36], for binary catalysts, $Pd_{30}Au_{70}$/C exhibited the best performance and thus here the feeding Pd/Au molar ratio was adopted to be 30:70. And thus, 0.47 mL of 12.00 mg mL^{-1} Pd^{2+}/EG solution was added; for Au/C, 2.55 mL of 9.56 mg mL^{-1} Au^{3+}/EG solution was added.). After stirring, 1.0 mol L^{-1} NaOH/EG was added into the solution to adjust the pH value of the above solution to be more than 12. After further stirring for 1 h, the slurry was microwave-heated (Nanjing Huiyan Corp., MZG800S) for 5 times in a 10 s-on/10 s-off pulse form and then re-acidified. The obtained black solid sample was washed by hot deionized water and dried in a vacuum oven at 80 °C for 12 h.

For the complete reduction of metal ions, the above prepared samples were further treated in a high-temperature oven with the mixture gas of H_2 (5%) and N_2 (95%) at 300 °C for 1 h. For the sake of comparison, Pd/C, Au/C, and PdAu/C catalysts were also prepared by the pulse microwave assisted polyol method without NH_3 modification. The detailed preparation process has been previously reported [35].

2.3. Chemico-physical characterization

All the products were characterized by *X-ray powder diffraction* (XRD) (Rigaku Co., Japan) with Cu K$_\alpha$ radiation (40 kV, 40 mA). The size and surface morphology of the particles were characterized by TEM (JEOL TEM-2010, HR). Before the measurements, the catalysts were dispersed in ethanol solution by ultrasonic water bath, later dried onto carbon coated copper grid. The chemical composition of the obtained products was determined by *scanning electron microscopy with energy dispersive X-ray spectroscopy* (SEM-EDX) (JEOL JSM-6330F). For the determination of metal content in the catalysts, *thermogravimetric* (TG) experiments were carried out with a Netzsch TG-209 analyzer in air with a flow rate of 50 mL min^{-1} and a temperature ramp of 10 °C min^{-1}.

2.4. Electrochemical analysis

All the electrochemical measurements were carried out using an AUT84480 instrument in a three-electrode system. Hg/HgO electrode (0.1 mol L^{-1} KOH) and platinum foil (1.0 cm × 1.0 cm) were
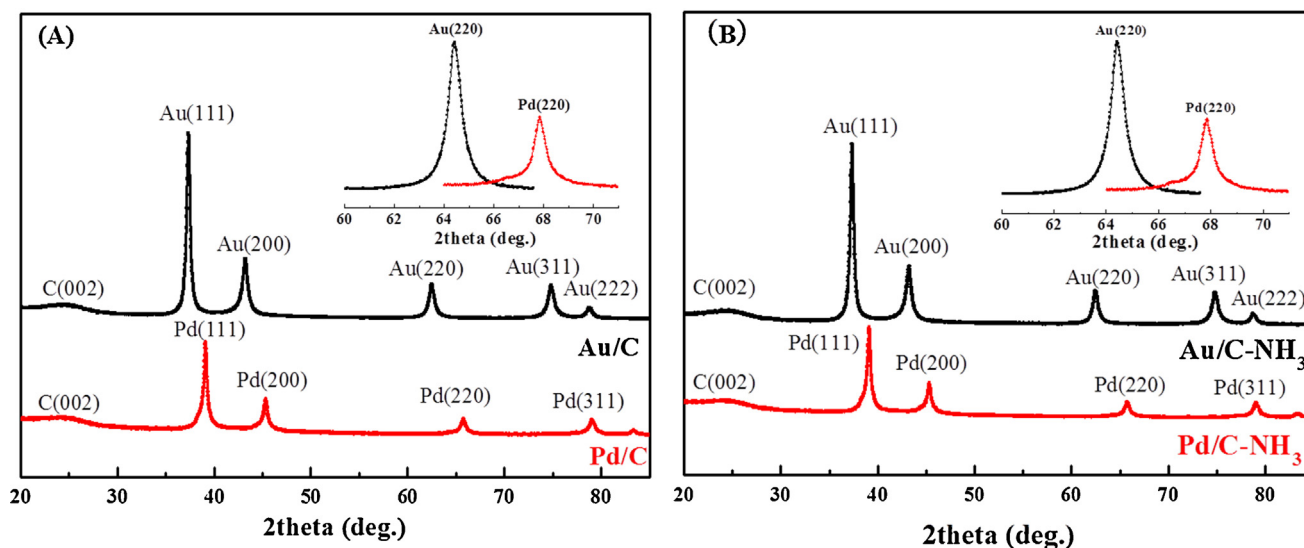

Fig. 1. XRD patterns for Pd/C and Au/C (A) and Pd/C-NH_3 and Au/C-NH_3 (B) catalysts and their corresponding detailed Pd or Au (2 2 0) peaks scanned at 1° min^{-1} as shown in the inset.

adopted as the reference and the counter electrodes, respectively. The working electrode was prepared by dispersing 5.0 mg of the as-prepared catalyst powder in 1.80 mL ethanol and 0.20 mL Nafion solution. The suspension was sonicated and stirred for ca. 30 min. Then, 10 μL of this ink was transferred onto the glassy carbon electrode with a diameter of 0.5 cm, and then the electrode was dried in an infrared lamp. The electrochemical tests of *cyclic voltammetry* (CV) and *chronoamperometry* (CA) were performed in the aqueous solution containing 0.1 mol L^{-1} NaOH and 20 mmol L^{-1} glucose. Before measurements, the electrolyte solution was saturated with

high-purity N_2 gas to provide an inert atmosphere. It should be noted that all the potentials are referred to Hg/HgO (0.1 mol L^{-1} KOH) reference electrode without specification.

3. Results and discussion

Fig. 1 shows the XRD patterns of Pd/C, Au/C, Pd/C-NH$_3$, Au/C-NH$_3$ and their corresponding detailed Pd or Au (2 2 0) peaks scanned at 1° min^{-1}. For all the catalysts, the diffraction peaks at around $2\theta = 25°$, correspond to the (0 0 2) reflections of graphitic
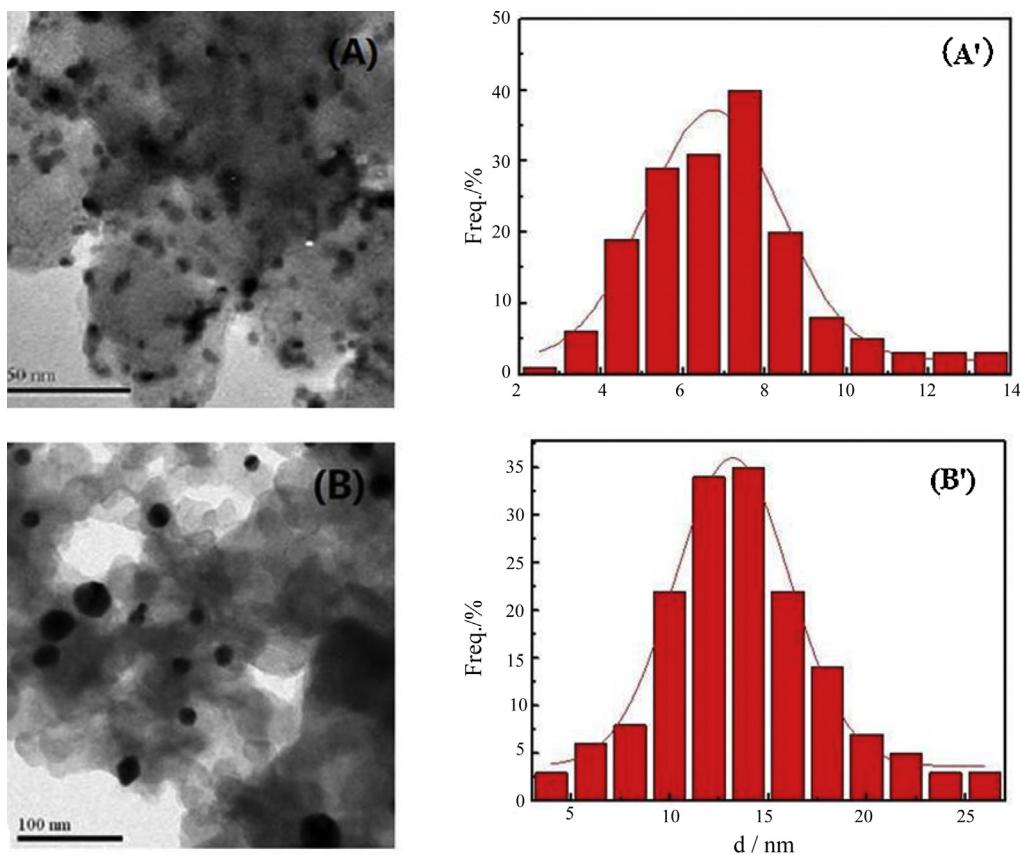

Fig. 2. TEM images of Pd/C-NH$_3$ (A) and Au/C-NH$_3$ (B) and their corresponding particle size distribution (A′ and B′).
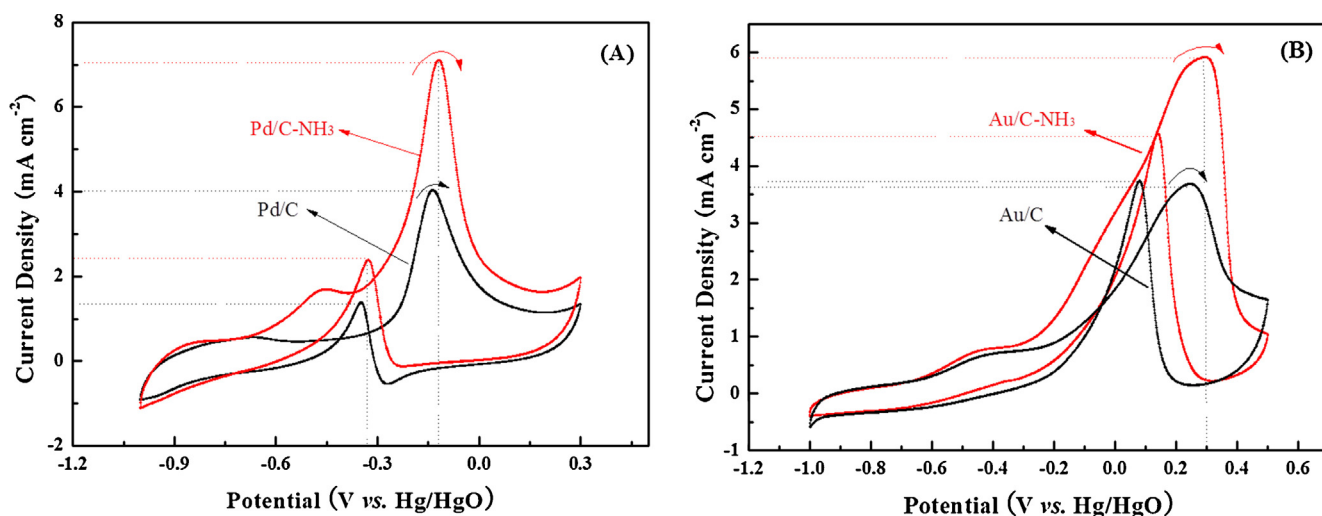

Fig. 3. Cyclic voltammetric curves of Pd/C and Pd/C-NH$_3$ (A) and Au/C and Au/C-NH$_3$ (B) in 0.1 mol L^{-1} NaOH aqueous solution in the presence of 20 mmol L^{-1} glucose at 50 mV s^{-1} and at 36.5 °C.

carbon. Moreover, all the samples present a typical fcc pattern. The metal particle size can be figured out from Pd (2 2 0) or Au (2 2 0) fine diffraction peaks shown in the inset of Fig. 1 using the Scherrer formula [39]. The crystallite sizes are 12.6 and 16.2 nm, for Pd/C and Au/C, and 10.5 and 9.1 nm for Pd/C-NH$_3$ and Au/C-NH$_3$, respectively. Obviously, the introduction of NH$_3$·H$_2$O to mediate the pulse microwave assisted polyol method could decrease the particle size of carbon supported Pd or Au catalysts. The TEM results for Pd/C-NH$_3$ and Au/C-NH$_3$ (Fig. 2) further verify the XRD results. The respective statistical particle size of Pd/C-NH$_3$ and Au/C-NH$_3$ is 6.7 and 12.5 nm, which is smaller than that of Pd/C and Au/C [35].

The electrocatalytic activities of Pd/C, Au/C, Pd/C-NH$_3$ and Au/C-NH$_3$ were then investigated by potentiodynamic voltammetric curves in the presence of 20 mmol L^{-1} glucose in 0.1 mol L^{-1} NaOH aqueous solution at a scan rate of 50 mV s^{-1} and at 36.5 °C as presented in Fig. 3. The maximum current peaks can be discerned for all the catalysts in the forward direction, which is due to the direct oxidation of glucose. At potentials beyond the peak, the current sharply decreases due to the formation of palladium/gold oxides. In the backward direction, the oxidation peaks are formed through the direct glucose oxidation at Pd or Au reduced from their oxide species. By comparing the CV curves on Pd/C, Pd/C-NH$_3$ and Au/C, Au/C-NH$_3$, it can be clearly seen that the introduction of NH$_3$·H$_2$O into the catalysts preparation can enhance the activity of Pd/C and Au/C, which could be due to the decreased particle size as discussed above.

Considering the effect of the atomic compositions [35], Pd$_{30}$Au$_{70}$/C-NH$_3$ was further synthesized by the NH$_3$ modified pulse microwave assisted polyol method. The XRD patterns for Pd$_{30}$Au$_{70}$/C-NH$_3$, Pd$_{30}$Au$_{70}$/C and their corresponding detailed
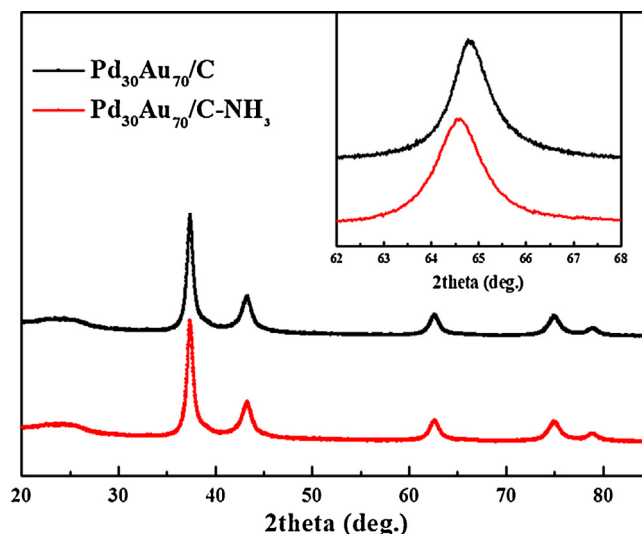
Fig. 4. XRD patterns for Pd$_{30}$Au$_{70}$/C and Pd$_{30}$Au$_{70}$/C-NH$_3$ and their corresponding detailed (2 2 0) peak scanned at 1° min^{-1}.

(2 2 0) peak scanned at 1° min^{-1} are shown in Fig. 4. Compared with the results as shown in Fig. 1, it can be seen that for single metal, the corresponding diffraction angles of Au/C are separated from those of Pd/C. While for binary catalysts, the diffraction peaks for Pd and Au are overlapped and they cannot be distinguished, indicating strong interactions between Pd and Au in PdAu binary catalysts. By comparing the diffraction patterns of Pd$_{30}$Au$_{70}$/C-NH$_3$
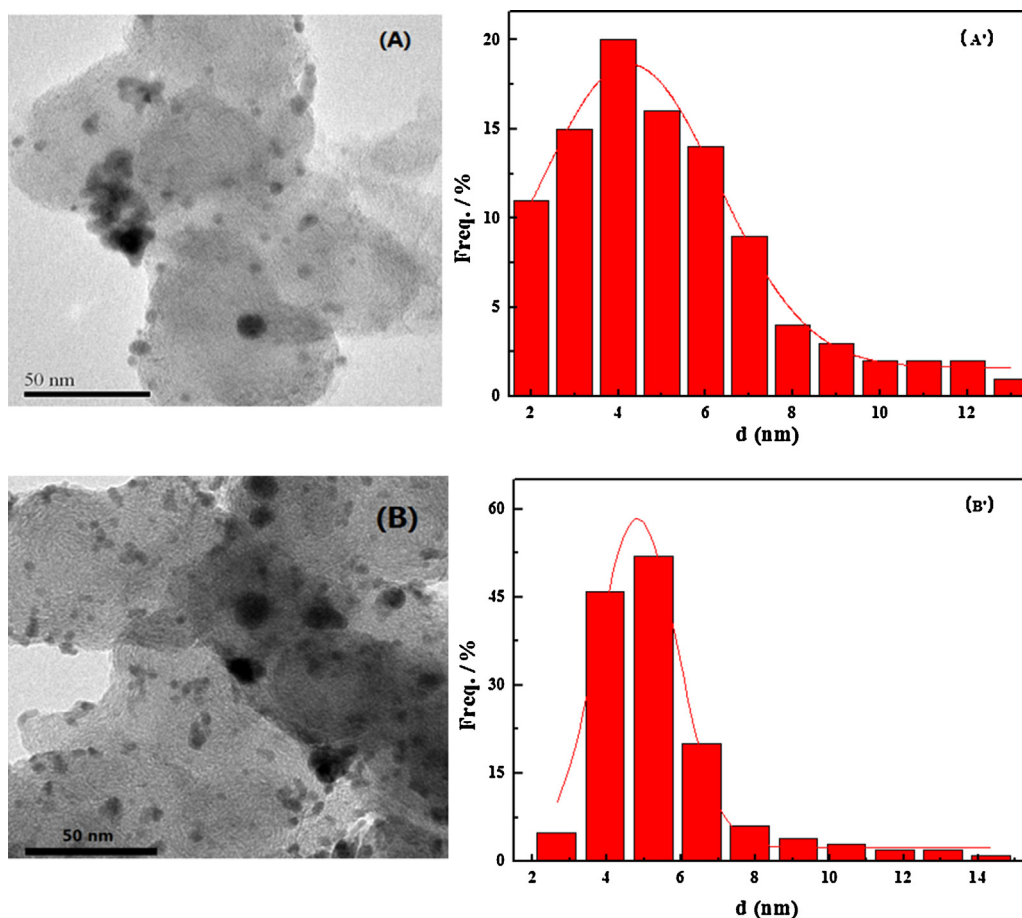

Fig. 5. TEM images of Pd$_{30}$Au$_{70}$/C-NH$_3$ (A) and Pd$_{30}$Au$_{70}$/C (B) and their corresponding particle size distribution (A′ and B′).

and $Pd_{30}Au_{70}/C$, it can be seen that the peaks are shifted to lower 2θ values, which could be due to the formation of PdAu alloy from the high temperature treatment in the former case. The calculated particle size of $Pd_{30}Au_{70}/C$-NH_3 is 5.4 nm, which is smaller than that of $Pd_{30}Au_{70}/C$ (7.1 nm) and all the single metal catalysts. Fig. 5 shows the TEM images of $Pd_{30}Au_{70}/C$-NH_3, $Pd_{30}Au_{70}/C$ and their corresponding particle size distribution. The metal particles are well dispersed on the carbon support, although there are some agglomerations. For $Pd_{30}Au_{70}/C$-NH_3, the statistical particle size is 4.4 nm, which is smaller than that of $Pd_{30}Au_{70}/C$ (4.8 nm). Moreover, it can be clearly seen that $Pd_{30}Au_{70}/C$-NH_3 has a much narrower

particle size distribution than $Pd_{30}Au_{70}/C$. The increased interaction between Pd and Au, decreased particle size and narrower particle size distribution could be beneficial for improving the activity of the catalysts.

The metal composite of the as-prepared $Pd_{30}Au_{70}/C$-NH_3 and $Pd_{30}Au_{70}/C$ was characterized by SEM-EDS. The EDS results (Fig. 6A and B) show that the atomic ratio of Pd and Au is 39:61 and 25:75, corresponding to $Pd_{30}Au_{70}/C$-NH_3 and $Pd_{30}Au_{70}/C$ respectively. The obvious deviation from the feeding Pd/Au molar ratio of 30:70 in $Pd_{30}Au_{70}/C$-NH_3 might be due to the easier reduction of Pd ions in H_2 atmosphere at high temperature. The metal content in the

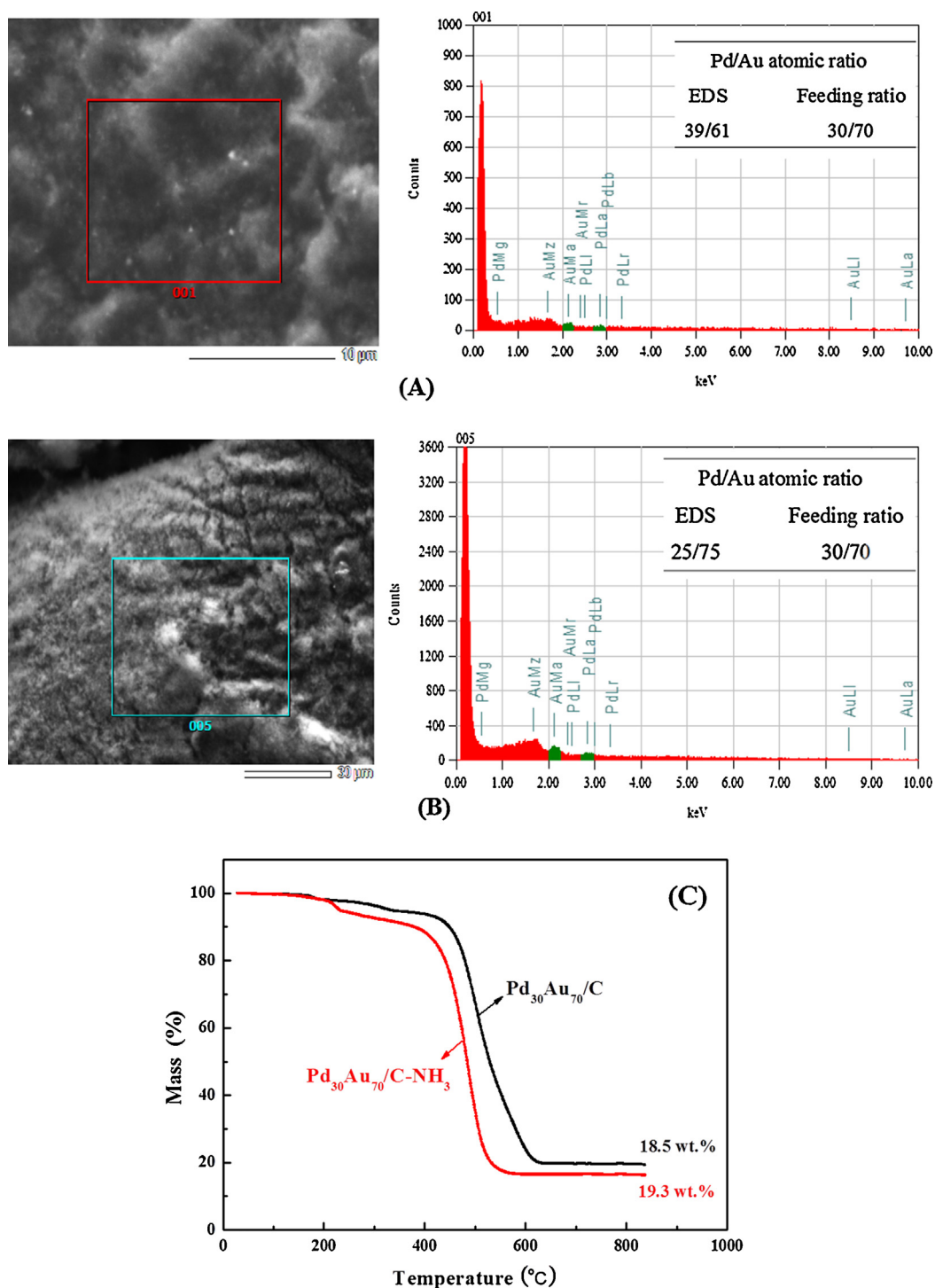Fig. 6. SEM-EDS micrographs of $Pd_{30}Au_{70}/C$-NH_3 (A) and $Pd_{30}Au_{70}/C$ (B) and their thermogravimetric curves (C).
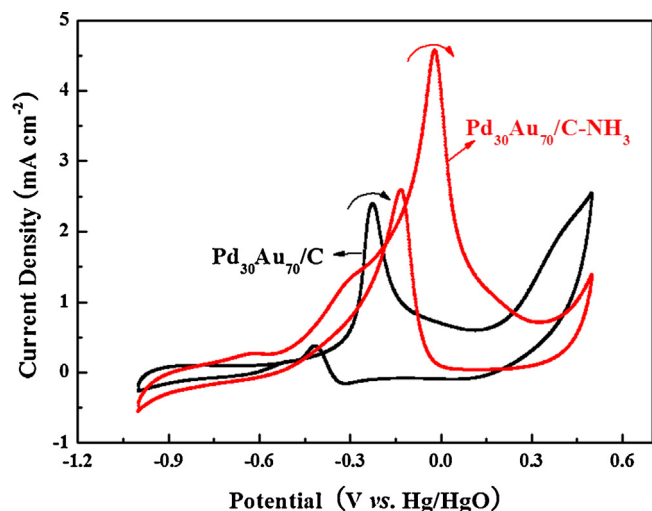
Fig. 7. Cyclic voltammetric curves of $Pd_{30}Au_{70}/C$ and $Pd_{30}Au_{70}/C-NH_3$ catalysts in $0.1\,mol\,L^{-1}$ NaOH aqueous solution in the presence of $20\,mmol\,L^{-1}$ glucose at $50\,mV\,s^{-1}$ and at $36.5\,°C$.

Fig. 8. Current–time record of $Pd_{30}Au_{70}/C-NH_3$ catalyst fixed on the rotating disk electrode ($1600\,rpm$) by a successive injection of $1\,mM$ glucose into $0.1\,mol\,L^{-1}$ NaOH solution at a regular interval time of $60\,s$. Applied potential: $0.02\,V$. Inset is the relationship between the current density and the added glucose solution.

catalysts is determined by TG to determine what extent the metal precursors can be reduced. As shown in Fig. 6C, below $200\,°C$, the weight loss for catalysts could be attributed to the desorption of water vapor and the residual EG. Therefore, the metal loading in the catalysts can be calculated from their TG curves after subtracting the weight of adsorbed water and the results are 19.3% and 18.5% for $Pd_{30}Au_{70}/C-NH_3$ and $Pd_{30}Au_{70}/C$ respectively, which is basically in accordance with the feeding weight ratio (20.0 wt.%).

The cyclic voltammetric curves of $Pd_{30}Au_{70}/C$ and $Pd_{30}Au_{70}/C-NH_3$ catalysts with $0.1\,mol\,L^{-1}$ NaOH aqueous solution in the presence of $20\,mmol\,L^{-1}$ glucose as the electrolyte are shown in Fig. 7. In the forward potential scanning, from the point of view of both current density and onset potential, $Pd_{30}Au_{70}/C-NH_3$ exhibits superior performance to $Pd_{30}Au_{70}/C$. The peak current density on $Pd_{30}Au_{70}/C-NH_3$ is almost double that on $Pd_{30}Au_{70}/C$. In the backward direction, $Pd_{30}Au_{70}/C-NH_3$ exhibits a little higher peak current density for glucose electrooxidation than $Pd_{30}Au_{70}/C$. While, the peak current density occurs earlier, which could be due to the lower oxidation degree of Pd and Au in the $Pd_{30}Au_{70}/C-NH_3$ (seen from the lower current density in the high potential limit).

In order to be applied in the electrochemical sensors, electrocatalysts are generally evaluated by monitoring the current response along with time at a fixed potential after addition of the analyte and possible interfering agents [40,41]. To assess the property of $Pd_{30}Au_{70}/C-NH_3$, the CA measurement was carried out at a fixed potential ($0.02\,V$) by a successive addition of the analyte ($1\,mM$ glucose each time) into $0.1\,mol\,L^{-1}$ NaOH solution at a regular interval time of $60\,s$. As shown in Fig. 8, after the injection of $1\,mM$ glucose into the electrolyte, a quick response of current ($<2\,s$) is observed, and then the current decreases to a relatively constant platform. The corresponding calibration plot for current versus glucose concentration is linear in the investigated glucose concentration range from 1 to 10 mM with a slope of $3.001\,\mu A\,mM^{-1}$. This value is bigger than that on PdAu/C obtained by the pulse microwave assisted polyol method ($2.372\,\mu A\,mM^{-1}$) [35], confirming the advantage of the NH_3 modified method for catalyst preparation.

Anti-interference ability has to be considered for the electrochemical sensor in detecting diabetes. The electrochemical response of the interfering species was investigated on $Pd_{30}Au_{70}/C-NH_3$ with the successive injection of analyte ($1.0\,mM$ glucose) and interfering agents including $0.1\,mM$ dopamine (DA), $0.1\,mM$ ascorbic acid (AA), $0.1\,mM$ uric acid (UA), $0.1\,mM$ fructose, $0.1\,mM$ sucrose, $0.1\,mM$ sodium gluconate, $0.1\,mM$ glucolactone, and
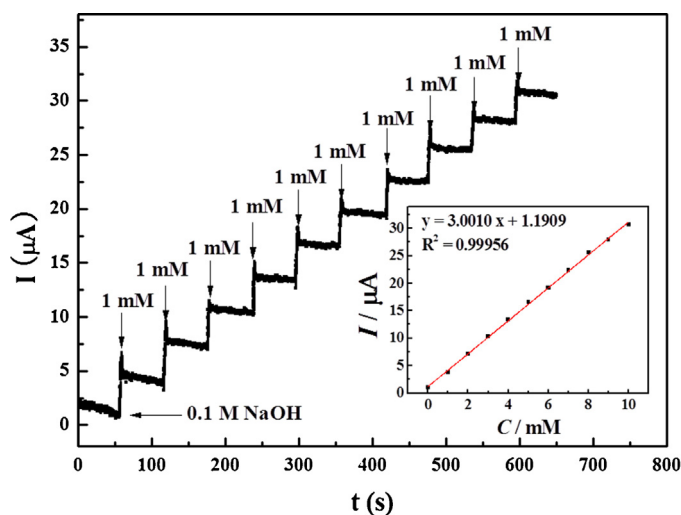
$0.15\,mol\,L^{-1}$. The above species and concentration were chosen based on the consideration that they are co-existing species with glucose in human blood and their corresponding concentrations except NaCl is about one thirtieth of glucose concentration. As shown in Fig. 9, once the glucose is injected, a quick increase in current is observed, which is consistent with the results in Fig. 8. While with the further successive injection of the interfering agents including dopamine (DA), ascorbic acid (AA) and uric acid (UA), fructose, sucrose, sodium gluconate, glucolactone, and NaCl at a regular interval time of $60\,s$, the current response is insignificant. After this series of injection, with another injection of $1.0\,mM$ glucose, the corresponding current increases sharply again. It can be inferred that the small quantity of DA, AA, UA, fructose, sucrose, sodium gluconate, glucolactone, and $0.15\,mol\,L^{-1}$ NaCl does not interfer the detection of glucose through electrochemical process. In other words, $Pd_{30}Au_{70}/C-NH_3$ exhibits high selectivity to glucose detection and good poison tolerance to Cl^-.
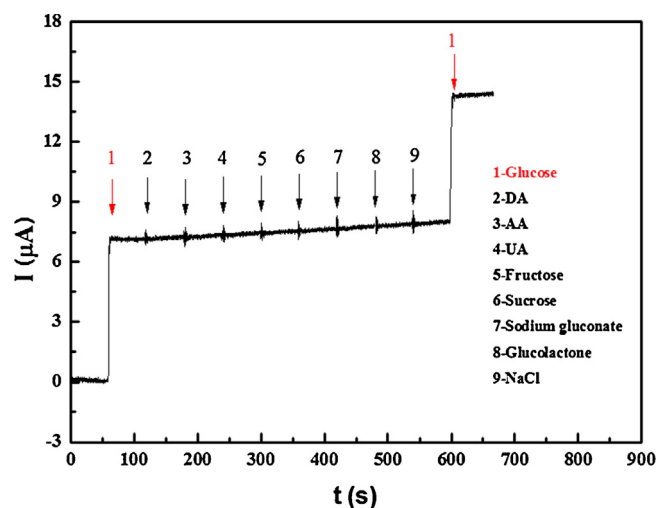

Fig. 9. Current–time record of $Pd_{30}Au_{70}/C-NH_3$ catalyst fixed onto rotating disk electrode ($1600\,rpm$) by successive injection of $0.1\,mM$ dopamine (DA), $0.1\,mM$ ascorbic acid (AA), $0.1\,mM$ uric acid (UA), $0.1\,mM$ fructose, $0.1\,mM$ sucrose, $0.1\,mM$ sodium gluconate, $0.1\,mM$ glucolactone, $0.15\,mol\,L^{-1}$ NaCl and $1\,mM$ glucose into $0.1\,mol\,L^{-1}$ NaOH solution at a regular interval time of $60\,s$. Applied potential: $0.02\,V$.

4. Conclusion

PdAu/C-NH$_3$ binary catalyst was synthesized by an NH$_3$ modified pulse microwave assisted polyol method, and then investigated for glucose electrooxidation. For the single metal catalysts, the particle size was effectively decreased through the complexing role of NH$_3$·H$_2$O to form [Pd(NH$_3$)$_4$]$^{2+}$/[Au(NH$_3$)$_4$]$^{2+}$ firstly, and thus their electrocatalytic activity for glucose electrooxidation was obviously improved. And this effect is also applicable to the PdAu/C binary catalyst.

The particle size of PdAu/C-NH$_3$ was evidently decreased, and its glucose electrooxidation performance was enhanced compared with PdAu/C obtained by unmodified method. Moreover, PdAu/C-NH$_3$ adopted for electrochemical sensors has the merits of rapid response, high sensitivity, and good tolerance to the interfering agents co-existing in the human blood with glucose. PdAu/C-NH$_3$ binary catalyst can be potentially applied for glucose electrochemical sensors or direct glucose fuel cells.

Acknowledgements

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